

The Conversion of Waste Scrubbing Liquor into Fertilizer

1 February 1995

Prepared by

KARL WESTBERG
Space and Environment Technology Center
Technology Operations
Engineering and Technology Group

Prepared for

SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE MATERIEL COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245

Contract No. F04701-93-C-0094

Programs Group

19960502 155

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION IS UNLIMITED



THE AEROSPACE
CORPORATION

El Segundo, California

THIS QUALITY INSPECTED 1

TECHNOLOGY OPERATIONS

The Aerospace Corporation functions as an "architect-engineer" for national security programs, specializing in advanced military space systems. The Corporation's Technology Operations supports the effective and timely development and operation of national security systems through scientific research and the application of advanced technology. Vital to the success of the Corporation is the technical staff's wide-ranging expertise and its ability to stay abreast of new technological developments and program support issues associated with rapidly evolving space systems. Contributing capabilities are provided by these individual Technology Centers:

Electronics Technology Center: Microelectronics, VLSI reliability, failure analysis, solid-state device physics, compound semiconductors, radiation effects, infrared and CCD detector devices, Micro-Electro-Mechanical Systems (MEMS), and data storage and display technologies; lasers and electro-optics, solid state laser design, micro-optics, optical communications, and fiber optic sensors; atomic frequency standards, applied laser spectroscopy, laser chemistry, atmospheric propagation and beam control, LIDAR/LADAR remote sensing; solar cell and array testing and evaluation, battery electrochemistry, battery testing and evaluation.

Mechanics and Materials Technology Center: Evaluation and characterization of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; development and analysis of thin films and deposition techniques; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; development and evaluation of hardened components; analysis and evaluation of materials at cryogenic and elevated temperatures; launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion; spacecraft structural mechanics, spacecraft survivability and vulnerability assessment; contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; lubrication and surface phenomena.

Space and Environment Technology Center: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation; propellant chemistry, chemical dynamics, environmental chemistry, trace detection; atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiative signatures of missile plumes, and sensor out-of-field-of-view rejection.

**THE CONVERSION OF WASTE SCRUBBING LIQUOR
INTO FERTILIZER**

Prepared by

Karl Westberg
Space and Environment Technology Center
Technology Operations
Engineering and Technology Group

1 February 1995

Programs Group
THE AEROSPACE CORPORATION
El Segundo, CA 90245-4691

Prepared for

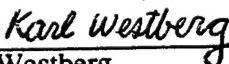
SPACE AND MISSILE SYSTEMS CENTER
AIR FORCE MATERIEL COMMAND
2430 E. El Segundo Boulevard
Los Angeles Air Force Base, CA 90245

Contract No. F04701-93-C-0094

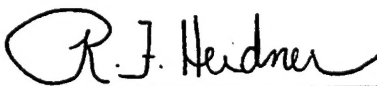
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION IS UNLIMITED


THE CONVERSION OF WASTE SCRUBBING LIQUOR
INTO FERTILIZER


Prepared


K. Westberg

Approved


R. F. Heidner, Director
Environmental Monitoring and
Technology Department


A. B. Christensen, Principal Director
Space and Environment Technology
Center


D. L. Nichols, Principal Director
Western Range
Space Launch Operations
Programs Group

The information in a Technical Operating Report is developed for a particular program and is not necessarily of broader technical applicability.

ABSTRACT

Used, unwanted scrubbing liquor consisting of an equimolar mixture of nitrate and nitrite dissolved in a highly alkaline solution ($\text{pH} > 13$) is now disposed of as a hazardous waste. However, this waste liquor can be converted into nitrate fertilizer by oxidizing the nitrite to nitrate with ozone and neutralizing the alkali with nitric acid to form a nitrate solution at $\text{pH} 7$. This report describes the chemical reactions, procedures, and equipment necessary for converting unwanted, partially depleted scrubbing liquor into nitrate fertilizer. It is concluded that the Hydrazine Waste Water Treatment System at Vandenberg Air Force Base can be used, with only slight modification, to both oxidize and neutralize waste liquor and thereby convert it to fertilizer.

Contents

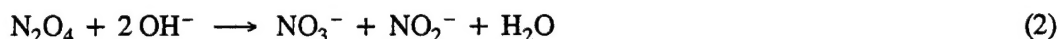
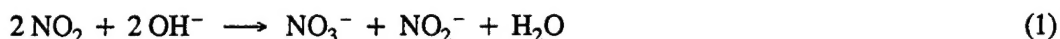
ABSTRACT.....	v
I. THE CHEMICAL COMPOSITION OF DEPLETED SCURBBING LIQUOR AND ITS CONVERSION TO FERTILIZER	1
II. THE REACTION BETWEEN OZONE AND NITRITE.....	7
III. NEUTRALIZATION OF WASTE SCRUBBING SOLUTION.....	13
IV. CHOOSING THE CORRECT EQUIPMENT AND PROCEDURES	17
REFERENCES AND NOTES.....	23

Figures

1. The equilibrium partial pressure of nitric oxide over a solution containing 30 mol/L nitrate and varying amounts of nitrite as a function of pH.....	3
2. A diagram of a packed column reactor.....	8
3. A diagram of one of the two bubble column reactors at the Hydrazine Waste Water Treatment System at VAFB	9
4. The concentrations of sodium nitrate and sodium sulfate in saturated solutions at 0°, 20°, 25°C.....	14

I. THE CHEMICAL COMPOSITION OF DEPLETED SCRUBBING LIQUOR AND ITS CONVERSION TO FERTILIZER

Liquid nitrogen tetroxide (N_2O_4) is a powerful oxidizer that is used in launch-vehicle rockets at Vandenberg Air Force Base (VAFB), Cape Canaveral Air Station (CCAS), and the Kennedy Space Center (KSC). Nitrogen tetroxide is a highly volatile liquid, producing vapors that contain a mixture of N_2O_4 and NO_2 . (NO_2 is nitrogen dioxide, which is a dark brown gas.) Some of these vapors end up as waste in a nitrogen or helium diluent whenever liquid N_2O_4 is loaded into a rocket at the launch site or transferred into a storage tank. At VAFB, CCAS, and KSC, these vapors are passed through a four-tower, packed-column scrubber, where they react with the scrubber liquor, which is a highly alkaline aqueous solution. A highly alkaline solution is one that contains a high concentration of hydroxide (OH^-). The overall stoichiometry of the chemical reactions of N_2O_4 and NO_2 in an alkaline solution is well-established. The *only* reaction products are nitrate (NO_3^-) and nitrite (NO_2^-), and these products are formed in *equal* amounts:



(Reactions 1 and 2 show the overall chemical stoichiometry, that is, the overall material balance; neither NO_2 nor N_2O_4 reacts directly with hydroxide to form nitrate and nitrite.¹)

An alkaline solution is usually prepared by dissolving either sodium hydroxide (NaOH) or potassium hydroxide (KOH) in water. Sodium hydroxide is used in the scrubbers at VAFB, CCAS, and KSC because it is cheaper than potassium hydroxide. Used, unwanted scrubbing solution is currently put into containers and buried in a Class A dump. Nitrate is an excellent fertilizer, while nitrite is less desirable. Therefore, if the nitrites in the used, unwanted scrubbing solution are oxidized to nitrate and the solution neutralized, then this waste scrubbing solution, so treated, could be used as a fertilizer. Many soils have too much sodium and too little potassium; consequently, the quality of the fertilizer would be much improved if the scrubbing liquor were made from potassium hydroxide instead of from sodium hydroxide. This report, however, describes only the treatment of waste scrubbing solution made from sodium hydroxide:

The scrubbing solution before use consists of 25 wt% NaOH and 75 wt% water. The hydroxide concentration in a 25 wt% NaOH solution is 8.0 mol/L (mole/liter), assuming complete ionization of the NaOH . The pH of this solution, as calculated from the formula $\text{pH} = -\log [\text{H}^+] = -\log (K_w/[\text{OH}^-])$, is $-\log (10^{-14}/8) = 14.9$. The pH that would be measured with a pH meter would be somewhat smaller. The initial volume of the scrubbing solution in the Titan IV Oxidizer Vapor Scrubber is about 1300 gallons, or 5,000 liters.² The capacity of the Oxidizer Vapor Scrubber used to service the Space Shuttle and the N_2O_4 storage tanks is about 750 gallons, or 2800 liters.³ As $\text{N}_2\text{O}_4/\text{NO}_2$ vapors dissolve and react in the scrubbing liquor, the volume of this liquor increases slightly, so that if the scrubbing liquor were used until completely depleted, that is, until all the hydroxide were consumed, then the concentrations of nitrate and nitrite in the solution would each be somewhat less than 4.0 mol/L. Actually, the solution is never used until complete depletion. For the scrubbers at the launch sites, the scrubbing liquor is considered spent and is not used again whenever the hydroxide concentration drops to between one-quarter and two-thirds of its initial value.⁴ The scrubbers servicing the N_2O_4 storage tanks are often used until the hydroxide in their liquor is about 90% to 95% depleted. Since the initial hydroxide concentration is 8.0 mol/L, and since the solution is diluted by N_2O_4 addition, waste scrubbing liquor

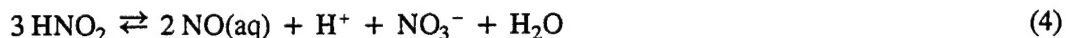
might contain between 5 and 0.5 mol/L OH^- and between 1.5 and 3.5 mol/L NO_2^- and NO_3^- .

Under a blanket of an inert gas, such as nitrogen, a highly alkaline solution of NO_3^- and NO_2^- is stable indefinitely. The alkaline scrubbing solution, however, is stored in the scrubber's sump tank under a blanket of air. Damschen and Martin⁵ bubbled oxygen through solutions containing dissolved nitrite and nitrous acid (HNO_2). They could detect no reaction between oxygen and nitrite, which indicates that in the absence of a catalyst, this is very slow reaction. Nevertheless, chemical analysis of depleted scrubbing liquor reportedly has indicated that there is more nitrate present than nitrite.⁴ If so, this would imply that some of the nitrite was oxidized to nitrate by oxygen in the air in spite of the very slow reaction rate. In the analyses presented in this report, however, it is assumed that the depleted scrubbing liquor has not been exposed to air for a sufficiently long time for appreciable nitrite oxidation to have occurred. Consequently, the nitrite and nitrate concentrations are taken to be equal. These concentrations can each be as large as 3.5 mol/L.

Highly alkaline nitrite solutions are stable indefinitely, but neutral or acidic nitrite solutions are not. In slightly alkaline, neutral, and acidic aqueous solutions, some of the nitrite reacts with hydrogen ions (H^+) to form nitrous acid (HNO_2):



Nitrous acid slowly disproportionates to form dissolved nitric oxide ($\text{NO}(\text{aq})$). The stoichiometry of this reaction is



Reaction 3 is very rapid and can be considered instantaneous, while reaction 4 is 20.6 kJ/mol endothermic and proceeds to equilibrium more slowly. In a dilute aqueous solution, the equilibrium constant for reactions 3 and 4 are $K_3 = [\text{HNO}_2]/[\text{NO}_2^-][\text{H}^+]$ and $K_4 = [\text{NO}(\text{aq})]^2[\text{H}^+][\text{NO}_3^-]/[\text{HNO}_2]^3$, where the brackets denote concentration in mol/L. The depleted scrubbing liquor, however, is a highly concentrated solution, and these expressions for K_3 and K_4 should be considered only approximately accurate. The value of the equilibrium constant K_3 is known to within 10%. Schwartz and White⁶ recommended $K_3 = 1.96 \times 10^3 \text{ L/mol}$ at 25°C. This recommendation was subsequently confirmed by the measurements of Park and Lee.⁷ The value of the equilibrium constant K_4 is not well established. Schwartz and White⁶ recommended $K_4 = 1.12 \times 10^{-4} \text{ mol/L}$ at 25°C, but this value may be accurate only to within a factor of ten.⁸

Nitric oxide (NO) is a toxic gas that is not particularly soluble in water. An aqueous solution containing dissolved nitric oxide will therefore continuously release nitric oxide gas. Nitric oxide is immediately dangerous to life and health⁹ when its concentration exceeds 100 ppm. The solubility constant, or Henry's law constant, for nitric oxide⁶ in a dilute aqueous solution is $H_{\text{NO}} = [\text{NO}(\text{aq})]/P_{\text{NO}} = 1.90 \times 10^{-3} \text{ mol L}^{-1} \text{ bar}^{-1} = 1.93 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$, where P_{NO} is the partial pressure of nitric oxide.

Figure 1 gives the results of calculations using the values of K_3 , K_4 , and H_{NO} given in the previous paragraphs. Plotted in this figure is the *equilibrium* partial pressure of nitric oxide P_{NO} above a solution containing 3.0 mol/L nitrate and varying amounts of nitrite as a function of pH. The nitrate concentrations of interest range from 1.5 mol/L to 7.0 mol/L. The nitrate could be as low as 1.5 mol/L in waste scrubbing liquor before any of the nitrite is oxidized to nitrate, and might be as high as 7.0 mol/L after oxidation of nitrite to nitrate is complete. The calculations in Figure 1 were performed only for $[\text{NO}_3^-] = 3.0 \text{ mol/L}$. Changing the assumed nitrate concentration from 3.0 mol/L to 1.5 mol/L or

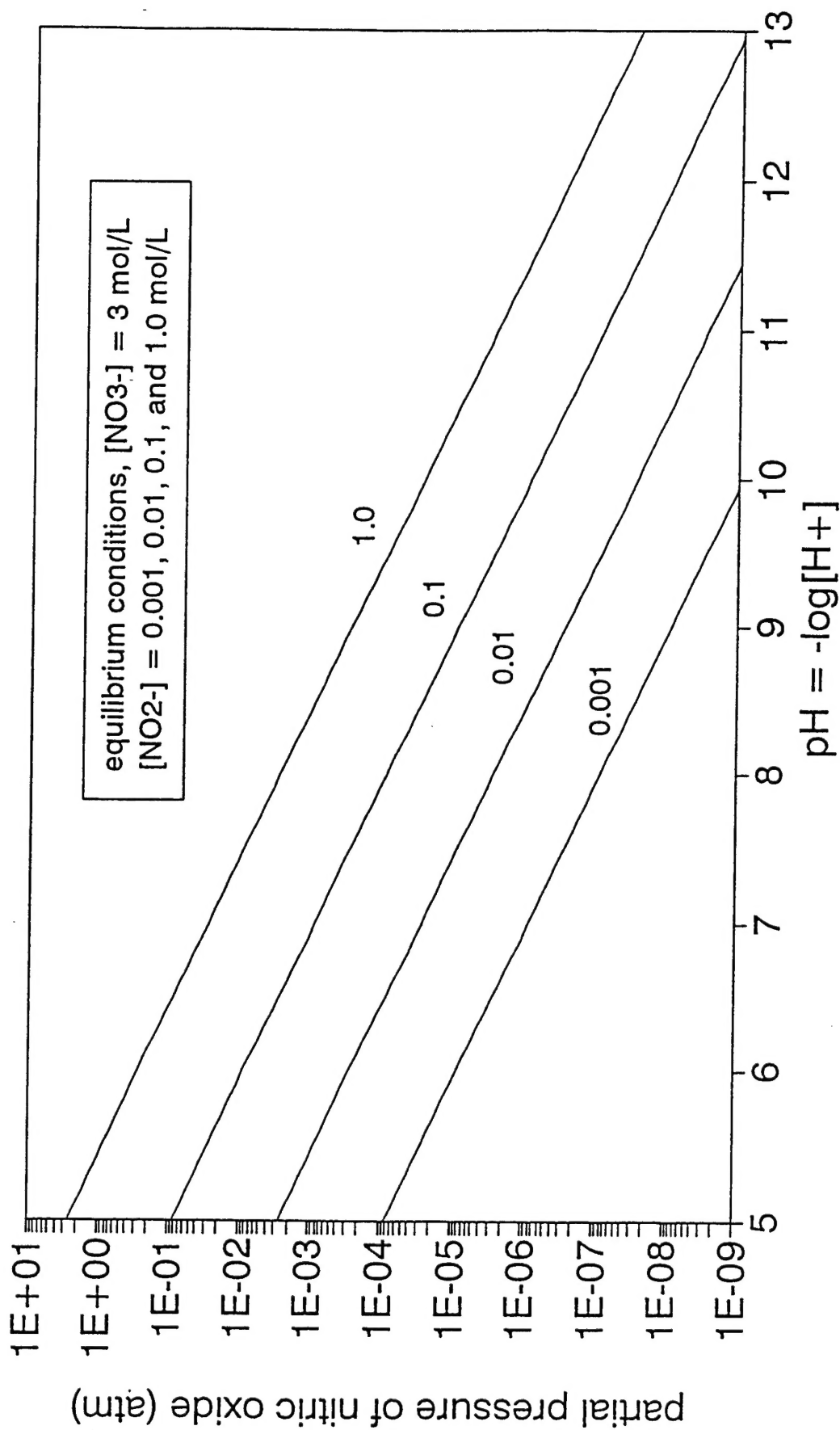


Figure 1. The equilibrium partial pressure of nitric oxide over a solution containing 3.0 mol/L nitrate and varying amounts of nitrite as a function of pH.

to 6.0 mol/L would change the calculated value of P_{NO} by only a factor of $\sqrt{2} = 1.41$, which is small in comparison to the uncertainty in the calculations.

The nitric oxide partial pressure calculated and plotted in Figure 1 is the partial pressure that might be measured in the ullage above a nitrite/nitrate solution stored in a sealed container. The nitric oxide partial pressure above a nitrite/nitrate solution in an open container would be much smaller. This is because the rate of release of gaseous NO from a nitrite/nitrate solution is slow in comparison to the rate of transport of vapors away from the surface of the solution by natural convection.

The calculated values of P_{NO} in Figure 1 are uncertain, partly because of the uncertainty in the value of K_4 and partly because the expressions used for K_3 , K_4 , and H_{NO} , namely, $K_3 = [\text{HNO}_2]/[\text{NO}_2^-][\text{H}^+]$ and $K_4 = [\text{NO}(\text{aq})]^2[\text{H}^+][\text{NO}_3^-]/[\text{HNO}_2]^3$, and $H_{\text{NO}} = [\text{NO}(\text{aq})]/P_{\text{NO}}$, are only uncertain approximations in concentrated solutions. It is difficult to estimate the error in the calculated values of P_{NO} , but a good guess might be that the error can be as large as a factor of 10, and that the true values of P_{NO} are more likely to be greater, rather than smaller, than the calculated values. Nevertheless, in spite of their large uncertainty, the calculated results in Figure 1 lead to some definite and pertinent conclusions:

- (1) A highly alkaline solution containing 1.5 to 3.5 mol/L each of nitrite and nitrate is stable. For example, as shown in Figure 1, the equilibrium partial pressure of nitric oxide over a pH 13 solution containing 1 mol/L NO_2^- and 3.0 mol/L NO_3^- is calculated to be only 3×10^{-8} atm, or 0.03 ppm. Spent scrubbing liquor is expected to have a pH near 14, which would make P_{NO} even smaller.
- (2) If a solution containing 1.5 to 3.5 mol/L each of nitrite and nitrate is neutralized to pH 7, unacceptably large amounts of nitric oxide will be produced. For example, the equilibrium partial pressure of nitric oxide over a solution containing 1 mol/L NO_2^- and 3 mol/L NO_3^- is calculated to be 0.03 atm (30,000 ppm). Because of the uncertainty in K_4 , the actual nitric oxide partial pressure could be even greater. To avoid unacceptably large values of P_{NO} , the nitrite in solution must be oxidized to nitrate before neutralization to pH 7.
- (3) Not all the nitrite, however, has to be oxidized to nitrate before neutralization can begin. For example, the pH of a solution containing 0.1 mol/L nitrite can be reduced from 14 to 11 (which is a thousandfold reduction in hydroxide concentration), and still the nitric oxide partial pressure would be less than 10^{-7} atm, or 0.1 ppm.
- (4) Not all the nitrite must be oxidized to nitrate to produce a chemically stable solution at pH 7. For example, the calculated equilibrium partial pressure of NO above a solution containing 0.01 mol/L NO_2^- (and 3.0 mol/L NO_3^-) is about 3×10^{-5} atm or 30 ppm. When the nitrite concentration is 0.001 mol/L, the calculated nitric oxide partial pressure is only about 1×10^{-6} atm, or 1 ppm.

Nitrite in aqueous solution is not highly toxic. Sodium and potassium nitrite are used to cure meats, such as sausages and hot dogs. Nitrite is a natural component of healthy soils, being produced by the oxidation of ammonia (NH_3); soil bacteria then oxidize the nitrite to nitrate.¹⁰ It should not be necessary, therefore, to reduce the nitrite concentration in the spent scrubbing liquor to vanishingly small levels before the spent scrubbing liquor is disposed of or used as a fertilizer. According to the Merck Index (11th edition, 1989), sodium or potassium nitrite is about 10 times more toxic to rabbits than is sodium or potassium nitrate. Reducing the nitrite concentration in the spent scrubbing solution to 0.01 mol/L would mean that the nitrate concentration in this solution would exceed the nitrite concentration by at least a factor of 300. The toxicity of the nitrite in such a solution would be negligible in comparison to the toxicity of the nitrate. For this reason, it would seem safe to assume that lowering the nitrite concentration to 0.01 mol/L would meet the requirements of the regulatory agencies, provided the pH

of the solution is near 7 and the equilibrium partial pressure of nitric oxide above this solution does not greatly exceed the values given in Figure 1. Of all the common chemical oxidizing agents, ozone seems to be the best choice for oxidizing nitrite to nitrate in an alkaline solution. As is discussed by Hank Judeikis in an Aerospace internal memorandum,¹¹ nitrite oxidation by hydrogen peroxide (H_2O_2) occurs only in acidic solutions, and oxidation by molecular oxygen (O_2) doesn't seem to occur at all. Oxidation by hyperchlorous acid (HClO) would produce sodium chloride, which is an undesirable ingredient of any fertilizer. (Adding a concentrated solution of sodium chloride to the soil is like adding concentrated sea water.)

The remainder of this report is divided into three sections. Section II discusses the reaction between ozone and nitrate; Section III, the neutralization of waste scrubbing solutions; and Section IV, choosing the right equipment and procedures.

II. THE REACTION BETWEEN OZONE AND NITRITE

The reaction between ozone and nitrite



has been studied repeatedly.^{5, 12-14} The reaction rate constant k_5 in a dilute aqueous solution is $1.6 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ at 9.1°C and $5.0 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25°C . The rate of reaction is independent of pH, and the only reaction product reported is nitrate. The heat of reaction $\Delta_r H^\circ$ is -243 kJ/mol at 25°C .¹⁵ (The negative sign denotes that heat is given off and the reaction is exothermic.)

Since ozone is a gas, the reaction of ozone with nitrite dissolved in an aqueous solution would have to take place in a gas-liquid reactor, such as a packed column reactor or a bubble column reactor. Figures 2 and 3 contain diagrams of these reactors. The time for ozone, uniformly dissolved in an aqueous solution, to react with nitrite is $1/(k_5[\text{NO}_2^-])$, which at 25°C is less than $200 \mu\text{s}$ when $[\text{NO}_2^-] > 0.01 \text{ mol/L}$. When $[\text{NO}_2^-]$ is 2.0 mol/L , the chemical reaction time is just $1 \mu\text{s}$. A reaction time of even $200 \mu\text{s}$ is short in comparison to gas-phase and liquid-phase transport times within a bubble column reactor, within a packed column reactor, or within most other gas-liquid reactors. For such reactors, the rate at which ozone reacts with nitrite in aqueous solution will be determined, at least in part, by the rate at which ozone is transported from the gas phase to the liquid/gas interface or by the rate of diffusion or mixing within the liquid phase, or by some combination of gas- and liquid-phase transport.

The Henry's law constant H_{O_3} for ozone dissolving in aqueous solutions is¹⁶

$$\begin{aligned} H_{\text{O}_3} &= [\text{O}_3(\text{aq})]/P_{\text{O}_3} \\ &= \{\exp \Delta_{\text{soln}} S^\circ / R\} \{\exp -\Delta_{\text{soln}} H^\circ / RT\} \end{aligned} \quad (6)$$

$$= \{\exp -(12.20 + 2.659 I_c)\} \{\exp ((2297 + 688 I_c)/T)\} \text{ mol L}^{-1} \text{ bar}^{-1} \quad (7)$$

where $\Delta_{\text{soln}} S^\circ$ is the standard entropy of solution; $\Delta_{\text{soln}} H^\circ$, the standard enthalpy; R , the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); T , the absolute temperature in kelvin; and I_c , the molar ionic strength ($I_c = \frac{1}{2} \sum c_i z_i^2$ where c_i is the molar concentration of each ion in solution and z_i is its electrical charge). The numerical values of $\Delta_{\text{soln}} S^\circ$ and $\Delta_{\text{soln}} H^\circ$ in Eq. (7) were determined by Kosak-Channing and Helz¹⁶ from their measurements of O_3 absorption in aqueous solutions having ionic strengths from 0 to 0.6 mol/L and temperatures from 5°C to 30°C . As expected, $\Delta_{\text{soln}} S^\circ$ and $\Delta_{\text{soln}} H^\circ$ were found to be independent of temperature, but to vary with ionic strength. Equation (7) is almost certainly accurate at higher-than-measured temperatures, at least up to 70°C or 80°C , but its accuracy at higher-than-measured ionic strengths is uncertain. Moreover, H_{O_3} depends on the chemical properties of the dissolved species, not just on its ionic strength. Equation (7) gives $H_{\text{O}_3} = 1.12 \times 10^{-2} \text{ mol L}^{-1} \text{ bar}^{-1}$ at 25°C for pure water ($I_c = 0$), and $H_{\text{O}_3} = 7 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1}$ at 25°C for a solution, such as waste scrubbing liquor, that has an ionic strength equal to about 8 mol/L . The value of H_{O_3} deduced from Eq. (7) may not be highly accurate when $I_c = 8 \text{ mol/L}$, but there is no doubt that ozone is much less soluble in concentrated aqueous solutions than in pure water. This reduced solubility must be considered when using measurements of ozone consumption in dilute solutions to predict ozone consumption in highly concentrated solutions. Regardless of ionic strength, the solubility of ozone decreases with increasing temperature. For example, Eq. (7) predicts that the solubility of O_3 in a solution having an ionic strength equal to 8 mol/L decreases by a factor of 16 as the temperature of the solution is increased from 25°C to 60°C . Ozone, of course, must dissolve in the waste scrubbing liquor before it can oxidize the nitrite

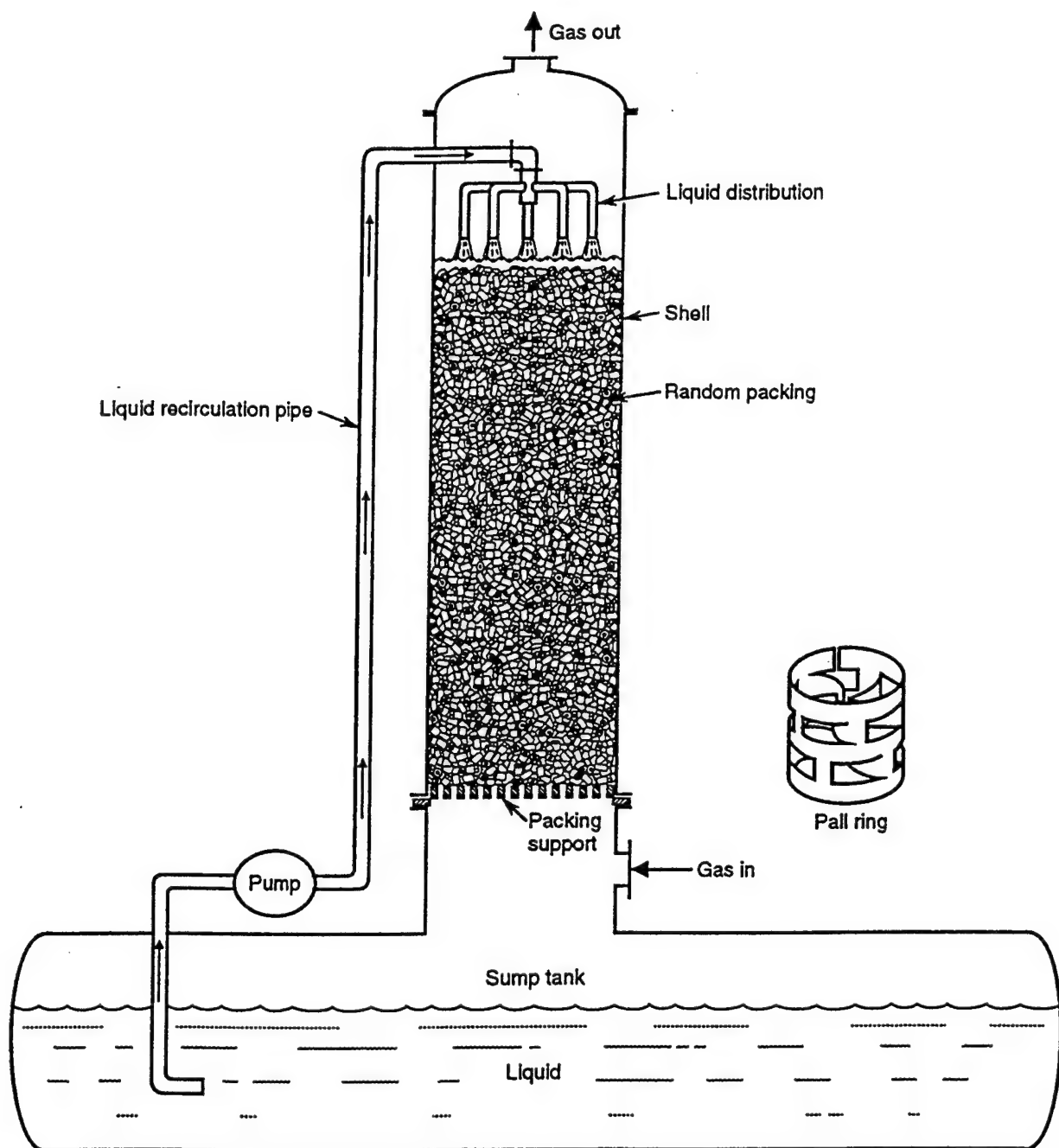


Figure 2. A diagram of a packed column reactor. This reactor is the most common type of gas-liquid reactor. Gas, in this case, a mixture of O_3 and O_2 , flows into the reactor from the bottom and exits at the top. Liquid, in this case waste scrubbing liquor, is pumped from the sump tank to the top of the column, where it is sprayed onto the packing material. The liquid flows down over the packing, returning to the sump tank. Packed column reactors are popular because the inlet gas can be at a low pressure, since the pressure drop across the column is small. A low inlet pressure is not a requirement, however, when using mixtures of O_3 and O_2 , since these mixtures are produced by ozonators that operate at about 30 psig. Several types of packing material are in common use. The oxidizer vapor scrubbers at KSC, VAFB, and CCAFS are filled with Pall rings.

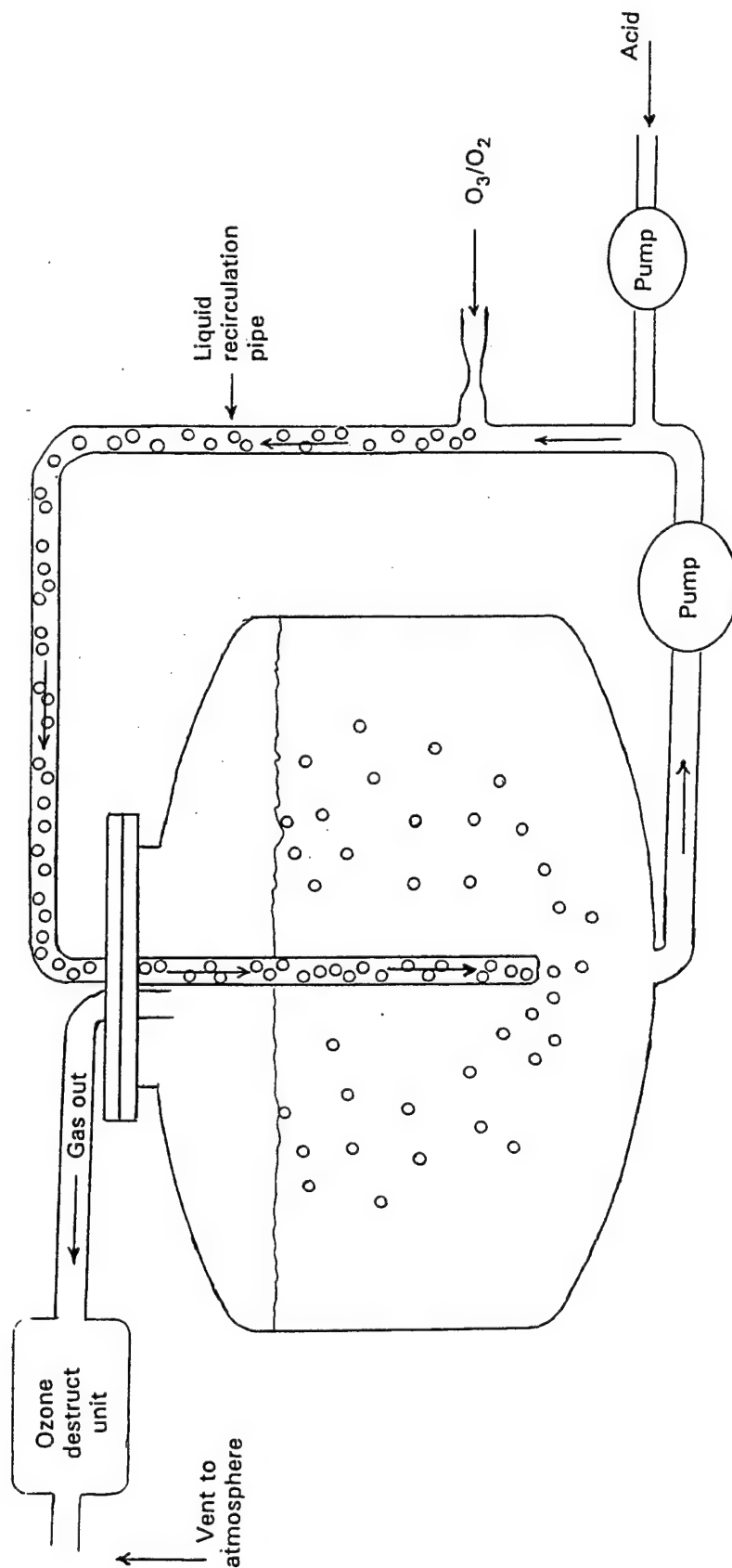
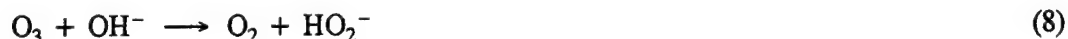


Figure 3. A diagram of one of the two bubble column reactors at the Hydrazine Waste Water Treatment System at VAFB. A bubble column reactor typically has a lower capital cost than other gas-liquid reactors. They are often more efficient than packed column reactors. The HWWTS bubble column reactors are used to oxidize and destroy waste hydrazine dissolved in water. They could be used, with only minor modifications, to oxidize and neutralize waste scrubbing liquor and so convert it to fertilizer. (This diagram is an idealization in that all the bubbles are depicted as having the same size instead of a range of sizes and frothing is ignored.)

in the liquor. The reduced solubility of ozone with increasing temperature means that the rate of oxidation of nitrite will decrease with increasing temperature. The magnitude of this decrease would depend on the relative importance of gas-phase and liquid-phase transport. If the overall reaction rate is limited primarily by the rate at which ozone molecules in the gas phase are transported to the gas-liquid interface, then a decrease in the solubility of ozone in the waste scrubbing solution would not greatly change the rate at which ozone oxidizes nitrite. But if the overall reaction rate is instead limited primarily by diffusion and mixing within the liquid phase, a decrease in O_3 solubility would slow down the rate of nitrite oxidation.

Ozone will also react with hydroxide, but at a slower rate



The rate constant¹⁷ for this reaction in dilute aqueous solution is $k_8 = 40 \text{ L mol}^{-1} \text{ s}^{-1}$ at 20°C , which is a factor of 10^4 smaller than the rate constant k_5 for the O_3/NO_2^- reaction. Reaction 8 is undesirable because it destroys ozone without oxidizing nitrite to nitrate. In addition, each HO_2^- ion produced in reaction 8 can react with and destroy an unknown number of ozone molecules via a not-yet-completely elucidated set of chain reactions.¹⁷ Reaction 8 and the subsequent reactions that destroy ozone can be made unimportant by keeping the concentration ratio $[\text{NO}_2^-]/[\text{OH}^-]$ sufficiently large. This can be done by continually adding acid to the waste scrubbing liquor as the nitrite concentration is being decreased by reaction with ozone. In addition, some acid may also have to be added to the waste scrubbing liquor before it is treated with ozone, especially if the initial hydroxide concentration is greater than the nitrite concentration. It is not possible at this time to specify how large the concentration ratio $[\text{NO}_2^-]/[\text{OH}^-]$ must be to make reaction 8 unimportant. This is because the relative rates of reactions 5 and 8 depend not only on the ratio $k_5[\text{NO}_2^-]/k_8[\text{OH}^-]$, but also on the rates of molecular diffusion and convective transport,¹⁸ which vary from reactor to reactor. As was discussed in section I and as will be discussed again in section III, the ratio $[\text{NO}_2^-]/[\text{OH}^-]$ can't be made too large; otherwise, the waste scrubbing liquor will release NO. The acceptable range of values for $[\text{NO}_2^-]/[\text{OH}^-]$ will vary with the gas-liquid reactor and can best be determined for each reactor of interest by performing tests in that reactor or perhaps in a pilot scale version of the reactor. The Air Force has funded two laboratory studies^{19,20} in which ozone was bubbled through synthetic, depleted scrubbing solution, until nitrite was completely or nearly completely oxidized to nitrate. In neither study, was any thought given to controlling the concentration ratio $[\text{NO}_2^-]/[\text{OH}^-]$, yet there was no good evidence reported in these studies that indicates that either reaction 8 was destroying an appreciable fraction of the ozone or that the solution was releasing NO. Therefore, it would seem that there might be a broad range of values for $[\text{NO}_2^-]/[\text{OH}^-]$ for which reaction 8 is unimportant and NO is not released.

Most chemical reaction systems produce at least a few unwanted by-products. This does not seem to be true for the reaction of O_3 with depleted scrubbing liquor. A literature search revealed no unwanted side reactions except with hydroxide, and by controlling the hydroxide concentration, it should be possible to make this reaction unimportant. Also the effect of the O_3/OH^- reaction, insofar as is known, is merely to destroy ozone, not to produce undesirable compounds that would degrade the quality of the final product, which is nitrate fertilizer. No by-products were reported in the two Air Force funded laboratory studies^{19,20} in which ozone was bubbled through an alkaline nitrite solution. Apparently, all that was observed was that ozone oxidized nitrite to nitrate, as expected.

Ozone is so reactive that it can't be purchased or stored for long. It is produced, as needed, by an ozone generator in which pure, dry oxygen (O_2) is passed through a silent electric discharge to produce a mixture of 1.5 to 3.5 mole% O_3 in O_2 . Let us consider in detail what happens when a gaseous mixture

containing 3.0 mole% O_3 in O_2 comes into contact with waste scrubbing liquor in a gas-liquid reactor, such as a bubble column reactor, a bubble-cap tray reactor, or a packed column reactor. If the reactor is efficient, all the ozone in the gas mixture will react with the nitrite in the waste scrubbing liquor, producing heat. The oxygen is nonreactive, and after passing through the reactor, it will be vented to the atmosphere. The oxygen, because it is dry, will cause some of the water in the waste scrubbing liquor to evaporate, thereby cooling this liquor. Initially, the heat from the O_3/NO_2^- reaction will be greater than the cooling by evaporation, and the temperature of the waste scrubbing liquor will rise. But an increased temperature will result in more evaporation and greater cooling. Eventually, a steady state will be reached in which the temperature will increase no more because the heat produced by chemical reaction is balanced by the cooling due to evaporation. This steady-state temperature can be easily calculated if we make a couple of reasonable approximations, namely, (1) the amount of heat lost by water evaporation greatly exceeds the amount of heat lost through the walls of the reactor and (2) the partial pressure of the water vapor in the oxygen leaving the reactor is equal to the vapor pressure of water above the waste scrubbing liquor as calculated from Raoult's law. The first approximation results in a calculated temperature that is somewhat too high; the second approximation, in a temperature that is too low. Together, both approximations should yield a fairly accurate estimate of the steady-state temperature within the reactor.

The vapor pressure of pure water P_v^* is adequately given by Eq. (9), which is an Antoine fit to data given in the current edition of the *Handbook of Chemistry and Physics*:

$$\log P_v^* = 5.195 - [1732/(T + 233.76)] \quad (9)$$

where P_v^* is in bar and T is in $^{\circ}C$. Equation (9) is accurate for $0 < T < 100^{\circ}C$. Raoult's law states that the vapor pressure of water P_v in an aqueous solution is

$$P_v = x_{H_2O(aq)} P_v^* \quad (10)$$

where $x_{H_2O(aq)}$ is the mole fraction of water in the solution. For waste scrubbing liquor, $x_{H_2O(aq)}$ is about 0.87. Under steady-state conditions, the heat produced by the O_3/NO_2^- reaction will be balanced by the cooling produced by evaporation, that is,

$$x_{O_3} \Delta_r H + \frac{x_{H_2O(aq)} P_v^* / P_t}{1 - x_{H_2O(aq)} P_v^* / P_t} \Delta_{vap} H = 0 \quad (11)$$

where x_{O_3} is the mole fraction of ozone in the O_3/O_2 mixture, $\Delta_r H$ is the molar heat of the O_3/NO_2^- reaction = -243 kJ/mol, $\Delta_{vap} H$ is the molar heat of vaporization of water = 44 kJ/mol, $x_{H_2O(aq)}$ is the mole fraction of water in the scrubbing liquor = 0.87 , P_t is the total pressure = 1.013 bar, and P_v^* is the vapor pressure of pure water, which is given by Eq. (9). Solving Eq. (11) for $x_{O_3} = 0.03$ gives a steady-state temperature of $56^{\circ}C$ ($133^{\circ}F$).

It would probably be desirable to operate at a lower temperature. The chemical reactor is less likely to experience corrosion at a lower temperature, and the efficiency of the reactor will most likely be greater because the solubility of ozone is greater at lower temperatures. It should not be difficult or costly to keep the scrubbing liquor $5^{\circ}C$ to $15^{\circ}C$ above ambient temperature.

III. NEUTRALIZATION OF WASTE SCRUBBING SOLUTION

Used, partially depleted scrubbing liquor is a highly alkaline solution, containing a high concentration of hydroxide (OH^-). Alkaline solutions can be neutralized by reaction with almost any acid that ionizes in water to produce hydrogen ions H^+ . The neutralization reaction is



The standard heat of neutralization, which is the enthalpy change of reaction 12 in a dilute aqueous solution, is -55.836 kJ/mol .¹⁵

Waste scrubbing liquor can be neutralized, for example, with nitric acid (HNO_3). The stoichiometry of this reaction is



The heat of this reaction in a dilute solution is the standard heat of neutralization (-55.836) plus the heat of dilution of nitric acid, which for a concentrated nitric acid solution (70 wt%) is -16.3 kJ/mol .¹⁵

If only nitric acid is used to neutralize the waste scrubbing liquor, the final product will be pure nitrate fertilizer, that is, a solution of sodium nitrate in water. The solubility of sodium nitrate in water is 6.7 mol/L at 0°C , 7.6 mol/L at 20°C , and 7.9 mol/L at 25°C . (These solubilities were computed from evaluated data given in refs. 21 and 22.) Virgin scrubbing liquor is 8.0 mol/L NaOH. This solution is diluted somewhat as it scrubs $\text{N}_2\text{O}_4/\text{NO}_2$ vapors. Addition of nitric acid will dilute it further. Evaporative losses during ozonation will make the solution more concentrated. The concentration of NaNO_3 in the final product usually should not exceed 6.7 to 7.0 mol/L, which will ensure that there will be no nitrate precipitation, even if the temperature of the solution drops to 5°C (41°F). Slightly higher concentrations ($\sim 7.4 \text{ mol/L}$) would be tolerable if it could be assured that the temperature of the solution would not drop below 20°C (68°F) or if the solution is to be pumped into an evaporation pond to remove the water and obtain sodium nitrate crystals. The concentration of NaNO_3 in the final product can be kept below 6.7 to 7.4 mol/L by neutralizing with nitric acid that is not too concentrated.

Sulfuric acid (H_2SO_4) also reacts with hydroxide:



The heat of this reaction in a dilute solution is the standard heat of neutralization (-55.836 kJ/mol) plus the heat of dilution of sulfuric acid, which is -95.3 kJ/mol for pure sulfuric acid. Sulfate, like nitrate, is a fertilizer; however, sodium sulfate, like most sulfates, is not highly soluble in water. The concentration of hydroxide in the waste scrubbing liquor is between 0.5 and 5.0 mol/L. So if sulfuric acid were used to neutralize this hydroxide, the concentration of sulfate after neutralization would be between 0.25 and 2.5 mol/L, assuming the water lost to evaporation during the ozone oxidation of nitrite were replaced. After oxidation of the nitrite is complete, the approximate concentration of nitrate (in mol/L) would be $8.0 - 2[\text{SO}_4^{2-}]$, or between 3.0 and 7.5 mol/L. Figure 4 gives the solubility of sodium sulfate in an aqueous solution containing between 1.0 and 8.0 mol/L sodium nitrate. The solubility is small at 20°C and decreases sharply with decreasing temperature. For example, at 20°C about 0.8 mol/L Na_2SO_4 can dissolve in a 4-mol/L NaNO_3 solution, while at 0°C only 0.1 mol/L Na_2SO_4 is soluble. Precipitation should be avoided within gas-liquid reactors. Consequently, only a small amount of sulfuric

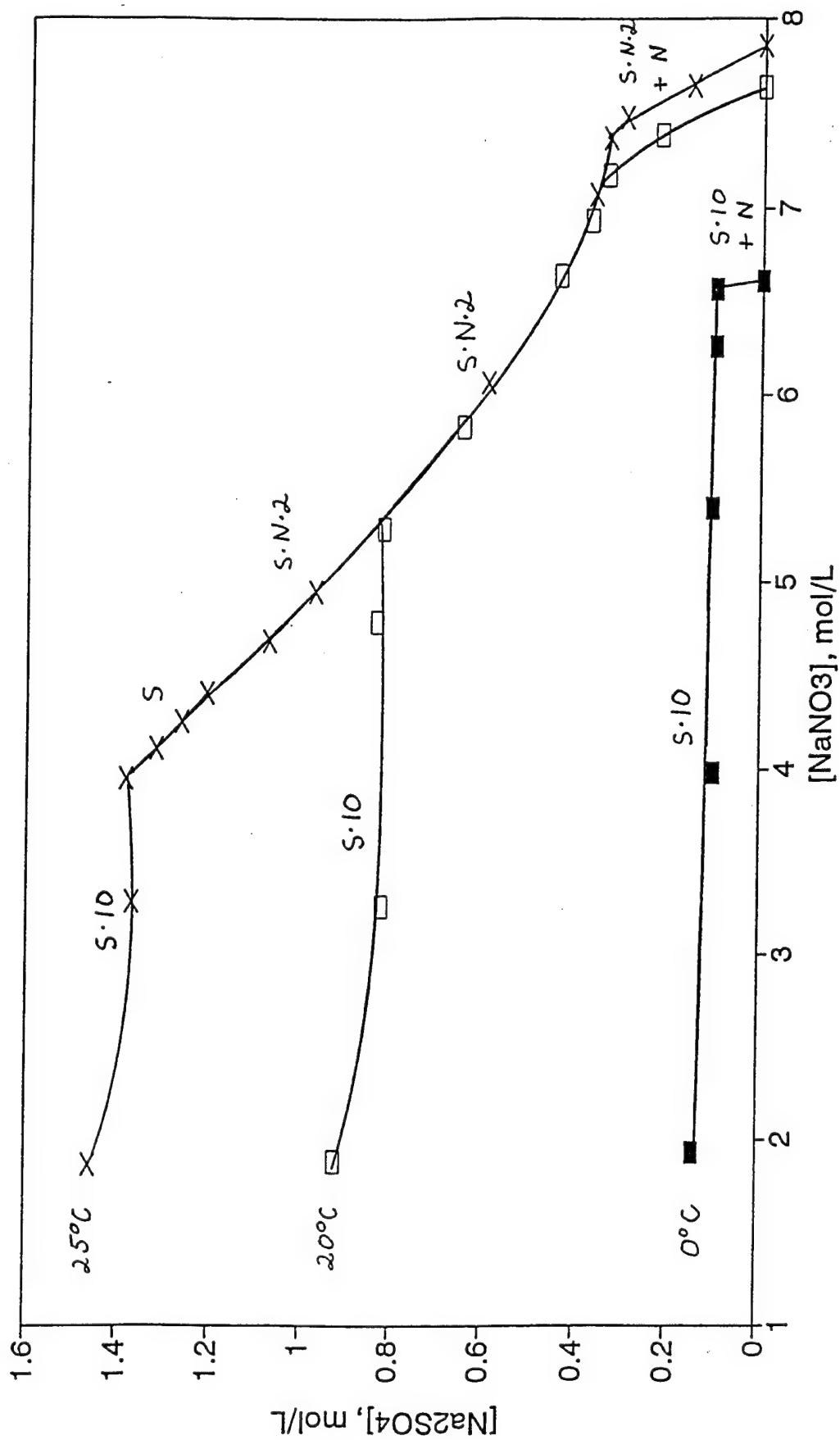
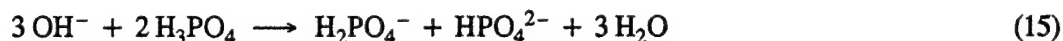


Figure 4. The concentrations of sodium nitrate and sodium sulfate in saturated solutions at 0°, 20°, 25°C. Above each curve is written the chemical composition of the precipitate: S = Na_2SO_4 , N = NaNO_3 , S·10 = $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, S·N·2 = $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. The data plotted in this graph are taken from ref. 21.

acid should be used to neutralize the hydroxide in these reactors. Nitric acid should be used to neutralize most of the hydroxide not neutralized by sulfuric acid because nitrates are highly soluble. Unless there is waste sulfuric acid available that must be disposed of, it would probably be more convenient to neutralize the waste scrubbing liquor using only nitric acid.

Orthophosphoric acid H_3PO_4 (which is often just called phosphoric acid) also reacts with hydroxide. The stoichiometry of the reaction depends upon the pH of the solution after reaction is complete. If the pH is near 7, the approximate stoichiometry is



That is, at pH 7, H_2PO_4^- and HPO_4^{2-} are present in roughly equal amounts, forming a buffered solution. Phosphates are excellent fertilizers; however, when phosphoric acid is added to a highly alkaline solution, a precipitate is formed. Phosphoric acid is much more soluble in mildly alkaline and neutral solutions.²¹ Consequently, some waste phosphoric acid can be added to the waste scrubbing liquor after it has been partially neutralized by another acid. A laboratory investigation would be required to determine the maximum amount that can be added.

Waste organic acid, such as waste acetic acid, could undoubtedly be added to the waste scrubbing liquor in small amounts, perhaps even in sizable amounts. Addition of hydrochloric acid (HCl), especially in sizable amounts, is undesirable because a solution of NaCl is formed, which is deleterious to all soils. Therefore, it seems the best approach would be to neutralize the waste scrubbing liquor with nitric acid, augmented with smaller amounts of waste sulfuric, phosphoric, and acetic acids that would otherwise be disposed of as hazardous waste. It might be acceptable to add a small amount of waste HCl as well. The waste acids, of course, cannot contain an unacceptably large concentration of dissolved heavy metals.

As is discussed in Section II, the scrubbing liquor should be partially neutralized as the nitrite is being oxidized to nitrate to minimize the importance of the O_3/OH^- reaction, which destroys ozone, without oxidizing nitrite. However, when concentrated acid is dumped into a concentrated alkaline nitrite solution, a cloud of brown gas is sometimes produced as the acid starts to mix with the alkaline nitrite solution. The brown gas is nitrogen dioxide. Nitrogen dioxide is released whenever the concentration of H^+ in the acid is much greater than the concentration of OH^- in the alkaline nitrite solution so that the solution becomes locally acidic as the acid mixes with it. If the solution stays acidic long enough, reactions 3 and 4 occur, releasing NO. A portion of the NO then is oxidized to NO_2 by atmospheric oxygen. If enough NO_2 is produced in this way, a cloud of brown gas will be visible. The release of NO_2 is undesirable and counterproductive. Scrubbing liquor is supposed to remove NO_2 , not release it.

The release of NO and NO_2 can be minimized or eliminated by using dilute acid, instead of concentrated acid, to neutralize the waste scrubbing liquor, and by keeping the scrubbing liquor agitated during neutralization. Agitation will increase the rate of mixing and thereby decrease the time any portion of the solution is locally acidic. Mixing will be more rapid if the acid is added slowly. Dilute acid also has the advantage of replenishing the water lost to evaporation during the ozone oxidation. The acid used to neutralize the waste scrubbing liquor should not be unnecessarily dilute; otherwise, the volume of the treated scrubbing liquor would become unacceptably large. Further investigation is needed to determine exactly when to add acid to the waste scrubbing liquor, how much acid should be added, and at what concentration. A laboratory investigation could begin to map out the concentrations of hydroxide, acid, and nitrite that lead to the release of NO and NO_2 .

IV. CHOOSING THE CORRECT EQUIPMENT AND PROCEDURES

Since the volume of the scrubbing liquor in the Titan IV Oxidizer Vapor Scrubber is 5,000 liters and the concentration of nitrite in the waste liquor from this scrubber is between 1.5 and 3.0 mol/L, the total amount of nitrite that must be oxidized is between 7,500 and 15,000 moles. Because one mole of ozone oxidizes one mole of nitrite, the total amount of ozone required is also between 7,500 and 15,000 moles or between 800 and 1600 lb. The ozonator at VAFB's Hydrazine Waste Water Treatment System (HWWTS) can produce 160 lb of ozone per day.^{23,24} Consequently, with this ozonator, between 5 and 10 days of continuous operation would be required to oxidize all the nitrite to nitrate if all the ozone produced by the ozonator reacted with the nitrite in the waste scrubbing solution.

Of course, bigger ozonators are available, and more than one ozonator can be used. Even so, the amount of nitrite that must be oxidized is so large that a chemical reactor is needed in which all or almost all the ozone that enters the reactor will react with the nitrite in solution to form nitrate. Fortunately, it should not be difficult to find or build such a reactor, since the rate constant k_5 for the ozone/nitrite reaction is large and the reaction proceeds almost as rapidly as ozone and nitrite can be brought into contact with each other.

The reaction between nitrogen dioxide (NO_2) and sulfite (SO_3^{2-}) in an alkaline solution is very similar chemically to the reaction between ozone and nitrite in an alkaline solution. Consequently, any chemical reactor in which the $\text{NO}_2/\text{SO}_3^{2-}$ reaction occurs rapidly and efficiently might well be a reactor in which the O_3/NO_2^- reaction occurs rapidly and efficiently. The $\text{NO}_2/\text{SO}_3^{2-}$ and O_3/NO_2^- reactions are chemically similar because NO_2 and O_3 have similar Henry's law constants and because their reaction rates are controlled largely by the rate of mixing within the reactor. At 25°C, nitrogen dioxide has a Henry's law constant¹ in pure water equal to about $1 \times 10^{-2} \text{ mol L}^{-1} \text{ bar}^{-1}$, which is essentially identical to the Henry's law constant for ozone in pure water, which is $1.12 \times 10^{-2} \text{ mol L}^{-1} \text{ bar}^{-1}$. The solubilities of NO_2 and O_3 are probably similar to each other in highly alkaline solutions as well. The rate constant²⁵ for the $\text{NO}_2/\text{SO}_3^{2-}$ reaction is about $3.5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, which is a factor of 100 larger than the rate constant for the O_3/NO_2^- reaction. This means that, like the O_3/NO_2^- reaction, the rate of the $\text{NO}_2/\text{SO}_3^{2-}$ reaction is largely controlled by the rate at which the reacting species come into contact with each other. Ozone and nitrogen dioxide have nearly equal diffusivities, both in the gas phase and in aqueous solution. Likewise, NO_2^- and SO_3^{2-} have comparable diffusivities in aqueous solution. Consequently, it would seem that a chemical reactor in which mixing is rapid enough for NO_2 to react efficiently with SO_3^{2-} is a reactor in which O_3 would react efficiently with NO_2^- .

Long and Fickey²⁶ showed experimentally that NO_2 reacts very rapidly with SO_3^{2-} in the NASA/Air Force oxidizer vapor packed column scrubber. As mentioned in Section I, this scrubber is ordinarily loaded with a 25 wt% NaOH scrubbing liquor and is used to remove waste $\text{N}_2\text{O}_4/\text{NO}_2$ vapors at high concentrations. In the tests performed by Long and Fickey, the usual scrubbing liquor was replaced with an alkaline sulfite solution consisting of 1.25 mol/L NaOH and 1.25 mol/L Na_2SO_3 . During some of these tests, the initial mole fraction of NO_2 , diluted in nitrogen, was less than 6,000 ppm, making reactions 1 and 2 unimportant. The oxidizer vapor packed column scrubber consists of four towers connected in series, but only one tower containing 0.55 m³ of packing material was required to remove almost all of the NO_2 . For example, when the combined NO_2/N_2 molar flow was 60 mol/min (50 SCFM), over 99% of the NO_2 was removed by reaction with sulfite in the first tower; when the flow was 240 mol/min (200 SCFM), 94% of the NO_2 was removed.²⁷ A diagram of a packed column scrubber or reactor is shown in Fig. 2.

Therefore, it seems that the oxidizer vapor packed column scrubber might be an efficient reactor in which to oxidize nitrite with ozone. A scrubber with only one or two towers instead of four towers would probably be adequate. It might be necessary to pass the output from the scrubber through an "ozone destruct unit" such as the one that is part of VAFB's Hydrazine Waste Water Treatment System. Acid could be continually added to the sump tank as the nitrite in the scrubbing liquor is oxidized to nitrate so as to keep the ratio $[\text{NO}_2^-]/[\text{OH}^-]$ large enough to make reaction 8 unimportant. When the oxidation of NO_2^- is considered complete, acid could again be added to the sump tank to neutralize the oxidized scrubbing liquor to pH 7. The solution would then be ready for use as fertilizer.

The Titan IV scrubber is equipped with a water-cooled heat exchanger that can be used to keep the temperature of its scrubbing liquor just a few degrees above the temperature of the cooling water. The scrubber that services the Space Shuttle does not have a heat exchanger because it was designed to handle smaller quantities of waste $\text{N}_2\text{O}_4/\text{NO}_2$ vapors. If a packed column reactor is used to treat waste scrubbing liquor, it too should probably be equipped with a water-cooled heat exchanger to prevent the temperature of the liquor from becoming too warm.

The oxidizer vapor packed column scrubbers are designed for gas flow rates between 50 and 400 CFM. An ozone generator that produces 3.0 mole% O_3 in O_2 at a flow rate of 60 SCFM (70 mol/min) would cost about \$150,000, not counting the costs of installation and providing cooling water. With this size ozonator, 5 days of continuous operation would be required to oxidize 5,000 L of solution initially containing 3.0 mol/L NO_2^- $[(3)(5000)/(0.03)(70) = 7,000 \text{ min} \approx 5 \text{ days}]$. Quicker operation could, of course, be achieved using a larger ozonator at a higher cost.

An alternative to a packed column reactor is a bubble column reactor, which is cheaper to build and no more costly to operate. Bubble column reactor are usually at least as efficient as packed column reactor of the same size. Unlike a packed column reactor, the pressure drop in a bubble column reactor is substantial since the reactive gas must bubble through a column of liquid. For many applications, a substantial pressure drop is unacceptable; however, ozone generators typically operate at a pressure of 30 psig, which is sufficient to bubble through a column of water several meters high. The IIT Research Institute (IITRI) designed a bubble column reactor for reacting NO_2 with SO_3^{2-} . IITRI's design was based on sound engineering principles and the results of pilot tests.²⁸ Bubbles are produced by a sparger having 4-mm diameter holes for the reactive gas to flow through. The bubble column reactor designed by IITRI for the $\text{NO}_2/\text{SO}_3^{2-}$ reaction should, with perhaps some modifications, be suitable for reacting O_3 with NO_2^- . The Hydrazine Waste Water Treatment System (HWWTS) at VAFB is also a bubble column reactor, or actually, a pair of bubble column reactors connected to a single ozone generator. The system has been in operation for three years and has performed successfully during that time. In the HWWTS reactors, ozone reacts with and destroys hydrazine fuels dissolved in water. As is discussed in the next several paragraphs, the HWWTS bubble column reactors and ozone generator could also probably be used to oxidize the nitrite in waste scrubbing liquor to nitrate.

Most bubble column reactors are equipped with a sparger having many small holes or orifices. Spargers having small holes can produce small bubbles, but they can also easily become plugged, especially when immersed in a very concentrated solution. The IITRI-designed sparger²⁸ has 4-mm dia holes or orifices, which are larger than is typical. The HWWTS bubble column reactors do not have spargers at all. Instead, as proposed to the Air Force by Farzad Baban of The Aerospace Corporation, the reactive gas, ozone, is injected directly into the bubble column's 3-inch OD liquid recirculation pipe. The liquid flow through this pipe, which is 150 gal/min, causes the gas that is injected into it to break up into bubbles of various sizes. Further breakup occurs and the bubbles become smaller as liquid and entrained gas are discharged into the HWWTS reaction tank. A diagram of the HWWTS bubble column reactor is shown in Fig. 3.

The two HWWTS reactors or reaction tanks are connected in parallel and can be operated independently. The single ozone generator supplies ozone simultaneously to both bubble columns. This ozone generator is from PCI Ozone Corporation, model HT50, list price \$77,000, and is capable of producing an O_3/O_2 mixture containing 4.5 wt% O_3 (which is equivalent to 3.0 mole% or 30,000 ppm O_3) at a molar flow rate of up to 30 SCFM (35 mol/min). As stated at the beginning of this section, it would take at least 10 days to convert 5,000 L of waste scrubbing liquor containing 3.0 mol/L NO_2^- to fertilizer using the HWWTS bubble column reactors with only the single ozonator that the HWWTS now has $[(3.0)(5000)/(0.03)(35)] = 14,000 \text{ min} \approx 10 \text{ days}$.

Up to 1125 gallons (4,250 L) of liquid can be treated at a time in each HWWTS bubble column reactor. Both reactors would therefore be needed to treat 5,000 L of waste scrubbing liquor. If the scrubbing liquor is divided equally between the two reactors, each reactor would contain 2,500 L of liquid, which is about 60% of its rated capacity. This rated capacity is for a liquid, such as water, that does not froth when gas is bubbled through it. Some frothing might be expected when bubbles are passed through a concentrated alkaline solution, but the amount of frothing is probably not very great otherwise frothing would have been observed and reported as a problem during either of the two Air Force sponsored studies in which ozone was bubbled through simulated waste scrubbing liquor.^{19,20} The volume of froth can be 1,250 L or about a foot high in the 89.5-inch ID reactor without the combined volume of liquid and froth exceeding 90% of the rated capacity.

VAFB's Hydrazine Waste Water Treatment System was constructed so that a variety of liquids, including dilute acid, could be pumped into the liquid recirculation pipe while O_3/O_2 is bubbling through the reaction tanks. Continual addition of the proper amount of dilute acid will keep the $[NO_2^-]/[OH^-]$ ratio always within acceptable limits. When the oxidation of NO_2^- is considered complete, more acid can be added to neutralize the oxidized scrubbing liquor to pH 7. The solution would then be ready for use as fertilizer.

Jim Kephart of The Aerospace Corporation, Vandenberg, has suggested delivering a jet of gaseous nitrogen into the liquid in the HWWTS bubble column. This nitrogen jet would agitate the liquid with the intent of breaking up any large bubbles of O_3/O_2 that might be present and thereby increasing the rate at which O_3 could be absorbed into the liquid. This seems to be a fine idea. A nitrogen jet would not only agitate the waste scrubbing liquor, it would also cool it by increasing the water evaporation rate. This could very well make an external heat exchanger, or the insertion of cooling coils, unnecessary. If the nitrogen flow were too great, there could be so many bubbles, so densely packed, that some of the small bubbles would coalesce into large ones. The criterion²⁹ for avoiding bubble coalescence in pure water is that the superficial gas velocity u should be less than 5 cm/s. The superficial gas velocity is the volumetric flow rate of the gas divided by the cross-sectional area of the bubbler in which it is flowing. For the HWWTS bubbler, $u = 0.2 \text{ cm/s}$; so it seems that it should be possible to add a sizable quantity of nitrogen before bubbles start to coalesce with each other. (Compressed air is cheaper than nitrogen, but is not a satisfactory substitute because air contains carbon dioxide, which reacts in alkaline solutions to form carbonate precipitates.)

The Hydrazine Waste Water Treatment System has only been used to treat water contaminated with small amounts of dissolved hydrazine (HZ), monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). Before the HWWTS was made operational at VAFB, it was tested at NASA's White Sands Test Facility.²³ There were 5 tests altogether. In each test, the combined concentration of hydrazine, MMH, and UDMH was 0.007 mol/L, which is several hundred times smaller than the expected amount of nitrite in waste scrubbing liquor. Nevertheless, it still is worth examining the results of these tests to see what can be deduced about the performance of this system as it relates to ozone oxidation of nitrite in waste scrubbing liquor.

No measurements were made of the amount of ozone that passed through the hydrazine wastewater unreacted. Thus, there is no direct way of determining if diffusion and mixing in the HWWTS bubble column reactors were rapid enough to remove all, or even most, of the ozone. There is some indirect evidence, however, that indicates that diffusion and mixing are not slow. The amount of O_3 that entered the reactor was measured in each test and so was the amount of HZ, MMH, and UDMH consumed. During the first one or two hours of test time, the ratio of O_3 molecules entering the reactor to the molecules of HZ, MMH, and UDMH destroyed was between 1.3 and 2.5, depending on test conditions. It is not known how many ozone molecules are required to oxidize one molecule of HZ, MMH, or UDMH to a product that resists further oxidation, but even if only one molecule can do the job, these results indicate that a sizable fraction of the ozone reacted in the bubbler, and maybe even all the ozone reacted.

The HWWTS bubble column reactor was originally built with porous metal spargers. Two tests were successfully completed using these spargers before they became plugged. One of these tests was later repeated with the sparger removed and the O_3/O_2 gas mixture injected into the liquid recirculation pipe, as is now done. As might be expected, the hydrazine fuels were oxidized more rapidly when the porous metal spargers were used because the bubbles were smaller; however, the rate of oxidation was not much faster. It took 9.5 hours to oxidize all three hydrazine fuels to undetectably small levels when using the spargers, while 11.5 hours were required without the spargers. Moreover, during the first 1.5 hours of testing, there was essentially no difference in the amount of hydrazine, MMH, and UDMH oxidized in either test. At the end of 1.5 hours, the combined fuel concentration was about 0.002 mol/L in both tests. The amount of oxidation was probably the same during the first 1.5 h of testing because all the ozone that entered the bubbler was consumed by reaction, regardless of whether spargers were present or absent. This implies that the HWWTS bubble column reactor without spargers is close to 100% efficient when the combined fuel concentration is greater than 0.002 mol/L.

The nitrite concentration in waste scrubbing liquor is at least several hundred times larger than the hydrazine concentration in wastewater. A higher concentration would tend to increase the rate at which ozone reacts. However, as was pointed out in Section II, the ozone solubility is less because the solution is more concentrated, making the reaction rate slower. Consequently, no definite conclusion can be made, but the hydrazine-wastewater tests seem to indicate that the efficiency of the HWWTS bubbler will be high, perhaps close to 100%, when it is used to oxidize waste scrubbing liquor.

From the available evidence, it seems that the chances are good that waste scrubbing liquor can be converted to nitrate fertilizer in a packed column reactor like the Titan IV Oxidizer Scrubber or in a bubble column reactor such as the one designed by the IIT Research Institute²⁸ or the bubbler that is part of the Hydrazine Waste Water Treatment System at VAFB. The HWWTS bubble column reactors can be used, with only minor modifications, to oxidize waste scrubbing liquor, neutralize it, and so make it into a fertilizer. The complete Hydrazine Waste Water Treatment System includes an ultraviolet photolysis unit and a tungsten catalytic tank that should be bypassed when treating the highly alkaline waste scrubbing liquor. The IITRI-designed bubble column reactor could also be used, provided its sparger is first tested to insure that it does not plug when used in waste scrubbing liquor.

The next big step might be to use the HWWTS bubble column reactors to treat a batch of waste scrubbing liquor and thereby determine efficiency of these bubble columns. This would also provide an opportunity to determine if there are any unforeseen difficulties in using ozone to convert waste scrubbing liquor to nitrate fertilizer. Performing a scaled-down pilot test first would be expensive because equipment would have to be purchased, assembled, and tested. Furthermore a pilot test cannot determine the speed and efficiency of diffusion and mixing within the HWWTS bubblers, because no scaled-down pilot test can

adequately simulate the fluid behavior within these bubble columns which contain no spargers, but rely on large scale turbulence in the fluid motion to create small bubbles. The HWWTS bubbler could easily be refitted with a sparger, such as the one designed by IITRI, should that prove necessary. Tests in the HWWTS bubble column reactor would provide more information than would any pilot test and would be cheaper.

Before the big step of using the HWWTS reactors to treat a batch of waste scrubbing liquor is taken, several smaller steps should be completed:

- (1) Check that the waste scrubbing liquor is compatible with all parts of the HWWTS with which it would come into contact.
- (2) Find and test analytic techniques that can be used in near real time to measure $[\text{OH}^-]$ and $[\text{NO}_2^-]$ in the waste scrubbing liquor as it is being processed.
- (3) Determine the chemical composition of the waste scrubbing liquor that is to be treated, including its impurities. Assess the likelihood of any of the impurities forming a precipitate while the scrubbing liquor is being treated.
- (4) Determine by laboratory test the highest acid concentration that can be used to neutralize alkaline nitrite solutions without release of more than trace amounts of NO and NO_2 .
- (5) Prepare a test plan that includes a specification of the measurements that are to be made during testing, the procedures that are to be followed, and the precautions that are to be taken. The measurements should include a determination of the maximum reactive gas flow that can be passed through each HWWTS bubbler. The concentration of nitrite in the waste scrubbing liquor is so great that it may well be desirable, at some time in the future, to operate the HWWTS bubblers with an O_3/O_2 flow greater than the current 30 SCFM and thereby reduce the time required to oxidize the nitrite to nitrate. If it is not possible to operate the present spargerless system at flows greater than 30 SCFM, it might be necessary to consider using a sparger with large holes that won't become plugged.

REFERENCES AND NOTES

1. S. E. Schwartz and W. H. White, "Kinetics of Reactive Dissolution of Nitrogen Oxides into Aqueous Solution" in *Trace Atmospheric Constituents*, S. E. Schwartz, editor (Wiley, New York, 1983), p. 1. [This book is vol. 12 in the Wiley series *Advances in Environmental Science and Technology*, J. O. Nriagu, series editor.]
2. R. Peterson, *Titan IV Oxidizer Vapor Scrubber System (OVSS), Final Engineering Report*, Report No. MCR-87-2621, Martin Marietta Astronautics Group, Denver (1987), section 6.
3. T. D. Reisert, "Nitrogen Tetroxide Vapor Scrubber Using a Recirculating Liquid" in *NASA Conference Publication 2049*, (1978); T. A. Murdock, *Performance Test of Hypergolic Propellant Vapor Scrubbers*, Report No. MCR-77-553, Martin Marietta Corporation, Denver (1977).
4. J. F. Kephart, unpublished memo (1994).
5. D. E. Damschen and L. R. Martin, *Atm. Environ.* **17**, 2005 (1983).
6. S. E. Schwartz and W. H. White, *Adv. Environ. Sci. Eng.* **4**, 1 (1981).
7. J. P. Park and Y. N. Lee, *J. Phys. Chem.* **92**, 6294 (1988).
8. In 1981, Schwartz and White⁶ recommended values of K_3 and K_4 that were consistent both with the available experimental measurements and with the data published in *The NBS Tables of Thermodynamic Properties*, which were also based on an analysis of the experimental measurements. A year later, NBS revised its Tables, making new recommendations for the thermodynamic properties of NO_2^- and HNO_2 that were consistent with a then new measurement of the absolute entropy of NO_2^- . The values of P_{NO} calculated using the new NBS recommendations are a factor of 26 larger than the values of P_{NO} calculated using the values of K_3 and K_4 recommended by Schwartz and White. Subsequent work by Park and Lee⁷ showed that the NBS recommendations cannot be correct, so the values of K_3 and K_4 recommended by Schwartz and White are adopted here. The NBS recommendations, while almost certainly inaccurate, do serve to point out that there is still a great deal of uncertainty about the exact value of K_4 .
9. U.S. Department of Health and Human Services, *NIOSH Pocket Guide to Chemical Hazards*, 162 (1990).
10. M. S. Ardakani, J. T. Rehbock, and A. D. McLaren, *Soil Sci. Soc. Amer. Proc.* **37**, 53 (1973).
11. H. S. Judeikis, *Treatment of Caustic Nitrite Solutions*, ATM 95(5662-02)-1, The Aerospace Corporation (1994).
12. J. H. Espenson and H. Taube, *Inorg. Chem.* **4**, 704 (1965).
13. V. A. Lunenok-Burmakina and T. M. Franchuk, *Ukr. Chim. Zh.* **36**, 1020 (1970). [Eng. Translation, *Ukr. J. Chem.* **36**, 40 (1970).]

14. S. A. Penkett, *Nature, Phys. Sci.* **240**, 105 (1972).
15. D. D. Wagman et al., *The NBS Tables of Chemical Thermodynamic Properties*, published as Volume 11, Supplement 2, of the *J. Phys. Chem. Ref. Data* (1982).
16. L. F. Kosak-Channing and G. R. Helz, *Environ. Sci. Technol.* **17**, 145 (1983).
17. H. Tomiyasu, H. Fukutomi, and G. Gordon, *Inorg. Chem.* **24**, 2962 (1985).
18. P. V. Danckwerts, *Gas-Liquid Reactions* (McGraw-Hill, 1970).
19. R. J. Dihu and B. J. Jody, *Oxidizer Scrubber Wastewater Treatment*, Final Report, Contract F04701-86-C-0002, IIT Research Institute, Chicago (June 1988).
20. D. D. Back, *Treatment of Nitrate and Mixed Nitrate/Sulfate Contaminated Waste Water*, Final Report, Contract F04611-93-C-0091, Mainstream Engineering, Rockledge, FL (March 1994).
21. W. F. Linke, *Solubilities*, Vol. II (American Chemical Society, 1965).
22. C. Synowietz, "Densities of Binary Aqueous Systems," in *Landolt-Börnstein*, New Series, Group IV, Vol. 1b, Kl. Schäfer and K. H. Hellwege, editors (Springer-Verlag, 1977).
23. R. E. Agthe, D. Johnson, and I. Smith, *Evaluation of the U.S. Air Force Hydrazine Waste Water Treatment System*, Test Report 628-001, NASA White Sands Test Facility, Las Cruces, NM (March 1992).
24. R. J. Lepley, Jacobs Services Company, Vandenberg AFB, private communication (November 1994).
25. R. E. Huie and P. Neta, *J. Phys. Chem.* **90**, 1193 (1986).
26. G. D. Long and E. W. Fickey, *Hypergol Oxidizer Vapor Scrubber Report, Phase IV & Phase V Test Results*, Report No. KSCE-824-0014, EG&G Florida, Kennedy Space Center (April 1989).
27. Calculated from the measurements of Long and Fickey,²⁶ correcting for the residual response of the chemiluminescent analyzer that was used to measure NO₂ mole fractions.
28. H. Dev and D. Jones, *Methodology for Reducing Emissions of Nitrogen Oxides (NO_x) by Treatment of a Waste Gas Stream*, IIT Research Institute, Chicago (October 1992).
29. Y. T. Shah, B. G. Kelkar, S. P. Godbole, and W. D. Deckwer, *AIChE Journal* **28**, 353 (1982).